D2

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C04B 38/00, B01F 3/00
C04B 35/00

A1

(11) International Publication Number: WO 93/04013

(43) International Publication Date: 4 March 1993 (04.03.93)

(21) International Application Number: PCT/GB92/01493

(22) International Filing Date: 12 August 1992 (12.08.92)

(30) Priority data:

9117421.9	12 August 1991 (12.08.91)	GB
9117422.7	12 August 1991 (12.08.91)	GB

(71) Applicant *(for all designated States except US)*: DYTECH CORPORATION LIMITED [GB/GB]; Stopes Road, Stannington, Sheffield S6 6BW (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : SAMBROOK, Rodney, Martin [GB/GB]; 11 Brookfields, Calver, Sheffield S30 1XA (GB). BINNER, Jonathan, Graham, Peel [GB/GB]; 41 Cranberry Close, West Bridgford, Nottingham NG2 7TQ (GB). SMITH, Robert, Terence [GB/GB]; 44 Hereward Road, Sheffield S5 7UB (GB). REICHERT, Jutta [DE/GB]; 6 Lyle Close, Melton Mowbrey, Leicestershire LE13 1HS (GB).

(74) Agent: SHAW, Laurence; George House, George Road, Edgbaston, Birmingham B15 1PG (GB).

(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).

Published
With international search report.

(54) Title: POROUS ARTICLES

(57) Abstract

A dispersion is formed by mixing particles of a refractory material and a liquid carrier to form a low viscosity composition which is foamed to form an article having green strength which is then dried and fired to form a porous article. The dispersion may include surfactants and a polymerisable monomer.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MN	Mongolia
AU	Australia	FR	France	MR	Mauritania
BB	Barbados	GA	Gabon	MW	Malawi
BE	Belgium	GB	United Kingdom	NL	Netherlands
BF	Burkina Faso	GN	Guinea	NO	Norway
BG	Bulgaria	GR	Greece	NZ	New Zealand
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	PT	Portugal
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland			SE	Sweden
CI	Côte d'Ivoire	KR	Republic of Korea	SK	Slovak Republic
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CS	Czechoslovakia	LK	Sri Lanka	SU	Soviet Union
CZ	Czech Republic	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America

GB-A-1272010 published in 1972 discloses a method in which a particulate ceramic material is mixed with an aqueous colloidal dispersion binder and gas generating agent to provide after activation by heating a structure containing fine pores uniformly distributed therein.

US-A-4505586 published in 1985 discloses a method of making a foamed product by incorporating a thickener, surfactant and binder while introducing bubbles into a slurry of a boehmite and water. The surfactant will be anionic or nonionic when the slurry is alkaline, and cationic or nonionic when the slurry is acidic. The binder may be a cement.

DE-A-3729371 published in 1988 discloses in very general terms a predominantly open-celled porous structure formed by mixing a particulate ceramic material, an aluminosilicate hydrogel, a surfactant and a gel strengthening agent. The surfactant is preferably a silicone glycol, and the gel strengthening agent is preferably silica fume.

GB-A-2213814 published in 1989 discloses making a foamed mixture by mixing a slip of silicon dioxide and a solution of a foaming agent, agitating and adding an alkaline magnesium or calcium compound.

POROUS ARTICLES

The invention relates to porous refractory articles and in particular to the manufacture thereof.

It is known to introduce gas into a mixture of particulate solids and a liquid carrier to form a foam which is then dried and fired to form a porous solid, typically ceramic.

FR-A-1003500 published in 1952 discloses a method in which a colloidal suspension of a clay in water is subjected to the formation of bubbles and setting simultaneously, to form, it is said, intercommunicating pores of uniform size. In the example, the deflocculating agent is soda which reacts with aluminium powder to generate in situ bubble-forming hydrogen gas and to cause flocculation.

US-A-3041190 published in 1962 discloses the use of a colloidal alumina having a boehmite structure and an organic foaming agent to form a wet foam. It is said that the use of colloidal alumina renders the foam resistant to collapse for at least 30 minutes.

EP-A-0330963 published in 1989 discloses a process in which an aqueous ceramic composition comprising particulate ceramic material and a film-forming polymer is frothed. Surfactants such as sulphonates and natural soaps may be used.

JP-A-0234583 published in 1990 discloses dispersing a foaming agent into a sol followed by gelling to produce a porous ceramic having a porosity gradient.

EP-A-0360244 published in 1990 discloses a method of making a structure having macropores in which a ceramic powder is mixed with a solution of a high molecular weight material such as celluloses, polyacrylamides etc.

It is one object of the invention to provide improved methods of making articles and the improved articles. In particular green bodies, i.e. those ready for firing, may be made more quickly, with better mechanical strength and handling and machining characteristics. The method offers the possibility of making articles which are larger in volume and/or of smaller pore size than by comparable routes. In addition, the methods may be applied to a wide range of starting materials and result in the formation of articles which consist essentially of the starting materials only.

According to the invention in one aspect there is provided a method of making a porous refractory article, the method comprising the steps of:

a) forming a dispersion comprising particles in a liquid carrier;

b) introducing gas into the dispersion; and

c) removing the liquid carrier to provide a solid article having pores derived from the bubbles,

<u>characterised in that</u> the dispersion has a critical viscosity selected to be below the level at which the introduction of gas cannot take place and above the level at which entrapped gas bubbles will tend to escape.

The viscosity of the dispersion will be low by which we mean that the viscosity must be less than that level at which the introduction of gas cannot take place and above the level at which entrapped gas bubbles will tend to escape. By the term "critical viscosity" is meant the corresponding viscosity at the critical stress value, see K.S. Chou, L.J. Lee, "Effects of Dispersants on the Rheological Properties and Slip Casting of Concentrated Alumina Slurries", <u>J. Amer. Ceram. Soc.</u> 72 (9) 1989, 1622-1627.

The critical viscosity of the dispersion will be in the range of from about 5 mPa.s, to about 1000 mPa.s preferably about 20 mPa.s to about 250 mPa.s. The preferred range is dependent on the method of gas entrapment. For entrapment by mechanical means e.g. stirring, the preferred range is about 20 mPa.s to about 200 mPa.s. For gas entrapment by mechanical means using a filter of defined pore size, the preferred range is about 50 mPa.s to about 250 mPa.s.

The dispersion comprises particles selected according to the intended end product in a liquid carrier and preferably is formulated so that the dispersion is essentially colloidal in nature. The average particle size will tend to be less than about 5 micrometres and preferably 95% of the particles will be less than about 2 micrometres. If the particles are larger than this size then the particles tend to settle or sediment. However, the particles can be much larger, say 100 micrometres or more, in which case agents will be present to control undesired settling; polymerisation of monomers is a suitable means for preventing settling.

The nature of the particles present will depend on the intended end use of the porous article to be formed. In the case of a ceramic it may be one or more of alumina, mullite, silicon carbide, silicon nitride, boron nitride, boron carbide, cordierite, silicas; zirconia, spinels, hydroxyapatite, magnesia and other metal xides, e.g. tin oxide or titanium xide or metal salts, e.g. nickel nitrate, nickel carbonate and the like.

Multi-component compositions may be used. Metals or alloys, e.g. ferrochrome, ferrosilicon, may be used. Dusts and other wastes from industrial processes may be used. The particles may be in the form of gelatinous precipitates. If necessary, powders may be ground or milled to achieve a suitable particle size distribution. This may be particularly useful if the particles are waste products from other processes. A high dispersion of the particles may also be prepared by a sol-gel technique.

The content of the solids in the dispersion will tend to be about 10% by weight as a minimum and about 90% by weight as a maximum; a preferred range is from about 40% to about 85% by weight.

Conveniently the liquid carrier is water but it may be organic, e.g. an alcohol, glycol or the like; or a mixture.

Where there is a risk that the formed dispersion will tend to undergo premature settling of solids it is preferred to add agents e.g. deflocculating agents so that the dispersion will be maintained. In the case of small particles, any premature settling or sedimentation will of course tend to disrupt the colloidal nature of the dispersion; the settling can take place by agglomeration of particles over time. The agent may be a deflocculating agent the nature of which will depend on the particles and the liquid carrier; for ceramic particles in water single or multiplecomponent surfactants (non-ionic, cationic or anionic), or carbohydrates may be used. Additives which adjust pH and polymers are also suitable agents. For large or small

particles polymerisable monomers may also be used.

The bubbles of gas may be introduced in any convenient way. For convenience and economy the gas is air. Preferred methods of introduction include:

1. subjecting the dispersion to a high intensity and/or high speed agitation while exposed to the atmosphere. The agitation is preferably carried out using a mixer, e.g. a mechanical mixer rotated at high speed. The agitation is carried out for sufficient period to introduce bubbles of air into the dispersion until expansion has been achieved according to the desired physical and other properties of the end product. The expansion ratio, i.e. the volume of foam formed compared to the volume of the starting dispersion, can be between about 10.1 and about 10, preferably between about 1.2 and about 1.7. The foaming of the dispersion may also be judged visually, i.e. because the foamed composition takes on the appearance of a meringue or pumice when sufficient air has been introduced. Other gases which can be introduced include nitrogen and oxygen;

2. the gas may be introduced by bubbling the gas through a filter of a defined p re size into the dispersion while being stirred. In this case the final pore size of the foam may be dependant on the pore size of the filter;

3. in a variation, high pressure gas is forced through a fine filter, then intimately mixed with the dispersion in a suitable chamber and the aerated mixture is then ejected from a nozzle;

4. the aerosol method may also be used, in this case the dispersion is housed in a pressurised vessel and gas is injected under pressure into the dispersion to produce a foam when ejected via a nozzle;

5. in another technique, a reactive gas generating substance may be added to the dispersion, the substance being selected to react with acid or alkali present with the dispersion to produce the required gas _in situ_, either when included or when subjected to agitation or heating.

The foaming characteristics of the dispersion may be controlled by the inclusion of a surfactant. The foam may be stabilised by the inclusion of foam builders. The addition of one substance may fulfil both roles.

A bonding or stabilising agent may be added to prevent collapse of the formed foam. It has been discovered that a deflocculating agent can fulfil this role also but any cationic, anionic or non-ionic surfactant can be considered.

Other additives may be present, e.g. liquefiers, viscosity control agents, reinforcing fibres or particles, accelerators,

retarders, colourants, and the like.

The foamed composition may be allowed or caused to acquire sufficient green strength to allow it to be moved from the parent container or mould. The composition may be subjected to drying to drive off the liquid. In the case of water the drying can be carried out at below about 100°C in an oven or using high frequency drying equipment. The drying step may be varied. For example, the drying may be done under reduced pressure to cause the foam to expand before the green strength is developed. The degree of expansion and hence the pore size of the foam will depend on the pressure selected. Drying at elevated temperature tends to cause a slight expansion of the foam. It is preferred to control the humidity during the drying step, to prevent uneven shrinkage and drying cracks, whereas if the polymerisable material is present in the dispersion this step might not need to be taken.

The dispersion may include other ingredients which play a role at the drying stage. Examples include binders such as resins, e.g. polyvinylchloride, gums, celluloses, and polymerisable materials to increase green strength. A specific class of such additives is organic monomers such as soluble acrylates and acrylamides. The additives are preferably dissolved in deionised water or other carrier liquid or a mixture to produce a premix solution, an initiator is add d to the dispersion before foaming and a catalyst after foaming. Elevated temperature can be a suitable substitute for the catalyst or both may be used together. The

resultant formed body after drying is relatively robust, and this addition is especially preferred when the article to be formed is of a complex shape.

Subsequent processing will depend on the nature of the intended article and the materials used; examples of suitable steps include shaping, e.g. machining, firing, impregnation of the pores with, e.g. catalysts and/or other agents. Porous articles made according to the invention can include: catalyst supports, flame supports; gas filters; airfresheners; ceramic armour; diesel particulate traps; insulation materials; artificial parts for the body; metal filters, reusable filters; liquid filters; storage and transportation for flammable and/or toxic materials, humidity sensors, chromatrography, filter candles for filtration of hot combustion gases, diaphragms, membranes, refractory separators, phase dividers and electrolytes for high temperature fuel cells.

The characteristics of the end product may be varied according to the conditions under which the method is performed. Where the contents of the solids in the dispersion is low, the viscosity will be reduced but the dispersion stability may be affected; lower viscosity dispersions tend to yield articles of lower density, i.e. higher pore content for a given solids content. By increasing the speed of stirring when introducing the gas bubbles the article formed will have a high pore content and a finer average pore size.

It is a feature of the invention that the final articles formed consist essentially of the starting refractory materials only, so avoiding the need for the presence of residual secondary materials, e.g. inorganic binders.

Our evaluations suggest that the pores size in the formed article can be controlled remarkably uniform. The pores may be closed and/or the porosity may be open. The true porosity may range from about 20% to about 95%.

In another aspect the invention provides a dispersion comprising particles in a liquid carrier characterised in that th dispersion has a critical viscosity selected to below that level at which the introduction of gas cannot take place and above the level at which entrapped gas bubbles will tend to escape.

The invention also includes a method of foaming a porous refractory article characterised by including a polymerisable monomer in the low viscosity dispersion of a particulate refractory material and water, foaming, drying and then sintering, whereby the article formed is relatively robust. The polymerisation preferably proceeds by crosslinking of reactive organic monomers. Examples include acrylates, such as ammonium acrylate or hydroxyethyl methacrylate; or the like. Preferably the monomers are dissolved in water or other liquid carrier to give a premix solution to which an initiator is added to cause free radical vinyl polymerisation to take place. Heat and/or a catalyst may be used to accelerate the process. In another

variation, the dispersion includes a monosaccharide such as galactose, which can be condensed to form a dimer, trimer or polymer, to have the same effect.

In another aspect the invention provides an article comprising a fired porous body comprising bonded refractory particles, characterised in that the body comprises essentially the refractory particles only.

In yet another aspect the invention provides an article having green strength comprising a foamed body of bonded refractory particles, characterised in that the article includes a polymerised monomer which will be removed when the article is fired.

In order that the invention may be well understood it will now be described by way of illustration only with reference to the following Examples.

Example I - Preparation of the dispersion or slurry

Different particulate materials as specified in Table I were each mixed with water and DECON 75 surfactant in the proportions specified and stirred for 5 minutes or until a homogeneous slip was obtained. (DECON 75 commercial formulations are believed to contain a polybasic dispersant and non-ionic surfactants). The slips were then subjected to a KERRY 150W 24000Hz ultrasonics unit set at 28 micrometres movement for 2 minutes to form an

essentially colloidal suspension.

Example II

A slurry comprising 80wt% alumina powder (Alcoa Grade A16 SG) with a mean particle size of less than 2 micrometres was prepared as in Example I. The slip was transferred to a Buchner funnel 120 mm diameter, with 10-16 micrometre pores and nitrogen bubbles through the funnel at a pressure of 0.4 bar for about 2 minutes. The nitrogen supply was then switched off and the foam slip transferred to a filter paper box and allowed to dry at room temperature for about 20 hours. The sample was then calcined by heating to 400°C, at a ramp rate of 1°C/minute and held at this temperature for 1 hour before heating to 1450°C at a ramp rate of 5°C and holding for 1 hour. The sample was then cooled to room temperature. The results are shown in Table I.

Example III

A slurry comprising 61wt% hydroxyapatite (Jesse Shirley Grade G1A) with a mean particle size of less than 3 micron was prepared as in the Example I. The slip was transferred to a Buchner funnel 120 mm diameter, with 10-16 micrometre pores and nitrogen bubbled through the funnel at a pressure of 0.4 bar for about 2 minutes. The nitrogen supply was then switched off and the foam slip transferred to a filter paper box and allowed to dry at room temperature for about 20 hours. The sample was then calcined by heating to 400°C, at a ramp rate of 1°C/minute and held at this

temperature for 1 hour before heating to 1300°C at a ramp rate of 5°C and holding for 1 hour. The sample was then cooled to room temperature. The results are shown in Table I.

Example IV

A slurry comprising 75wt% partially stabilised yttria zirconia (Zirconia Sales Grade HSY-3) was prepared as in Example I. The slip was transferred to a Buchner funnel 120 mm diameter, with 10-16 micrometre pores and nitrogen bubbled through the funnel at a pressure of 0.4 bar for about 2 minutes. The nitrogen supply was then switched off and the foam slip transferred to a filter paper box and allowed to dry at room temperature for about 20 hours. The sample was then calcined by heating to 400°C, at a ramp rate of 1°C/minute and held at this temperature for 1 hour before heating to 1500°C at a ramp rate of 5°C and holding for 1 hour. The sample was then cooled to room temperature. The results are shown in Table I.

Example V

A slurry comprising 75wt% alumina powder (Alcoa Grade A16 SG) with a mean particle size of less than 2 micrometre was prepared as in Example I. The slip was then transferred to a 400 ml beaker and stirred using a paddle blade rotating at 1250 rev/min for 5 minutes to entrap air. The foamed slip was then

transferred to a filter paper box and placed in an oven at 36°C for 10 hours. The sample was then calcined by heating to 400°C, at a ramp rate of 1°C/minute and held at this temperature for 1 hour before heating to 1450°C at a ramp rate of 5°C and holding for 1 hour. The sample was then cooled to room temperature. The results are shown in Table I.

Example VI

A slurry comprising 71.4wt% partially stabilised yttria zirconia (Zirconia Sales Grade HSY-3) was prepared as in the Example I. The slip was then transferred to a 400 ml beaker and stirred using a paddle blade rotating at 1250 rev/min for 5 minutes to entrap air. The foamed slip was then transferred to a filter paper box and allowed to dry at room temperature for about 20 hours. The sample was then calcined by heating to 400°C, at a ramp rate of 1°C/minute and held at this temperature for 1 hour before heating to 1500°C at a ramp rate of 5°C and holding for 1 hour. The sample was then cooled to room temperature. The results are shown in Table I.

Example VII

A slurry comprising 78wt% alumina powder (Alcoa Grade A16 SG) with a mean particle size of less than 2 micrometre was prepared as in Example I. The slip was then transferred to a 400 ml beaker and stirred using a paddle blade rotating at 1250 rev/min f r 5 minutes to entrap air. The foamed slip was then

transferred to a filter paper box and allowed to dry at room temperature for about 20 hours. The sample was then calcined by heating to 400°C, at a ramp rate of 1°C/minute and held at this temperature for 1 hour before heating to 1450°C at a ramp rate of 5°C and holding for 1 hour. The sample was then cooled to room temperature. The results are shown in Table I.

Example VIII

A slip was formed of 50 g of hydroxyapatite, 2.74 ml of DECON 75 and 50 ml of deionized water. The slip was subjected to ultrasonic agitation at an amplitude of 24 millimetre for 2 minutes. Agarose, 1 g, was added. The slip was heated to 90°C and then stirred in air at 1200 rpm for 3 minutes. The foamed slip was poured into a filter paper box and then cooled in a refrigerator to 8°C, allowing the agarose to set. The set foam was dried to a green strength and then sintered at 1350°C for 1 hour. The product had a mean pore diameter of 24 micrometre.

Example IX

Alumina, ammonium acrylate monomer, misethylenebisacrylamide crosslinking agent, ammonium polycarboxylate dispersant, the ammonium salt of polymethacrylic acid, Teepol surfactant and water were mixed to form a low viscosity slip which was subjected to ultrasonic vibration in the manner of Example 1. Ammonium persulphate initiator was stirred in. The slip was transferred to a beaker and stirred using a Kenwo d mixer (175W power at

speed setting 3 for about 5 minutes) when a foam of uniform consistency was obtained. Triethanolamine catalyst was stirred in for about 30 seconds. The foam started to polymerise and was left for 24 hours at room temperature, and then dried at 60°C in an oven. The sample was then sintered by being heated at 400°C for one hour, then at 1450°C for two hours.

Example X

A premix solution was made of acrylamide, methylenebisacrylamide and water. Alumina and DECON 75 were added and the whole stirred until a smooth slip was obtained. The slip was subjected to ultrasonic vibration for 2 minutes. The low viscosity slip was transferred to a beaker and ammonium persulphate was added. The slip was stirred using a mixer to generate a foam. Tetramethylethylenediamine was stirred in for a minute and left to homogenise the mix. It was transferred to a beaker and left to stand for 14 hours. The sample was then removed, and heated to 70°C in an oven. The sample was then heated slowly to 1450°C at which it was left for one hour. The sample has 81% porosity.

Example No.	Ceramic material	Method of gas entrapment	Wt% of material	DECON in mg/g of material	Drying Temp. °C	Sintering Temp. °C	Critical visc. /mPas	Density %
II	Al_2O_3	F	80.0	30.0	RT	1450	101.4	7.0
III	HA	F	61.0	50.0	RT	1300	64.4	13.0
IV	ZrO_2	F	75.0	50.0	RT	1500	182.0	19.0
V	Al_2O_3	S	75.0	50.0	36.0	1450	23.0	16.0
VI	ZrO_2	S	71.4	50.0	RT	1500	27.1	16.0
VII	Al_2O_3	S	78.0	70.0	RT	1450	45.0	39.0
VIII	HA	S	48.0	60.0	Setting - 8 Drying - RT	1350	15.0	52.0
IX	Al_2O_3	S	68.0	*	60	1450	180.0	7.0
X	Al_2O_3	S	59.0	40.0	70	1450	103.0	19.0

F = Buchner funnel, S = Mecahnical Stirrer; HA = Hydroxyapatite; RT = Room Temperature
* = text

CLAIMS

1. A method of making a porous refractory article, the method comprising the steps of:

a) forming a dispersion comprising particles in a liquid carrier;

b) introducing gas into the dispersion; and

c) removing the liquid carrier to provide a solid article having pores derived from the bubbles,

characterised in that the dispersion has a critical viscosity selected to be below the level at which the introduction of gas cannot take place and above the level at which entrapped gas bubbles will tend to escape.

2. A method according to Claim 1, characterised in that the critical viscosity is from about 5 mPa.s to about 1000 mPa.s.

3. A method according to Claim 1 or 2, characterised in that the critical viscosity is from about 20 mPa.s to about 250 mPa.s.

4. A method according to Claim 1, 2 or 3 characterised in that the critical viscosity is in the range of from about 20 mPa.s to about 200 mPa.s and the bubbles are introduced by mechanical means.

5. A method according to Claim 1 or 2, characterised in that the critical viscosity is from about 50 mPa.s to about 250 mPa.s and the bubbles are introduced using a filter of a defined pore size.

6. A method according to any preceding Claim, characterised in that contents of the solids in the dispersion is about 10% to about 90% by weight, preferably about 40% to about 85% by weight.

7. A method according to any preceding Claim, characterised in that the average particle size of the particles in the dispersion is less than about 5 micrometres.

8. A method according to Claim 7, characterised in that the average particle size of the particles in the dispersion is less than about 2 micrometres.

9. A method according to any of Claims 1 to 6, characterised in that the average particle size ranges up to about 100 micrometres and agents are present to control undesired settling.

10. A method according to any preceding Claim, characterised in that a deflocculating agent selected to control and maintain the bubbles is present in the dispersion.

11. A method according to any of Claims 1 to 10, characterised in that a gas is introduced into the dispersion by agitation at high speed.

12. A method according to any of Claims 1 to 10, characterised in that the gas is introduced by bubbling through a filter of defined pore size into the dispersion while being agitated.

13. A method according to Claim 12, characterised in that high pressure gas is forced through a fine filter, then intimately mixed with the dispersion in a suitable chamber and the mixture ejected from a nozzle.

14. A method according to any of Claims 1 to 10, characterised in that the dispersion is housed in a pressurised vessel and gas is injected under pressure into the dispersion to produce a foam when ejected via a nozzle.

15. A method according to any of Claims 1 to 6, characterised in that a gas generating substance is added to the dispersion and caused to generate gas *in situ*.

16. A method according to any preceding Claim, <u>characterised in that</u> the liquid is removed by drying under reduced pressure.

17. A method according to Claim 16, <u>characterised in that</u> the dispersion includes at least one additive to exert an effect at the stage of removing the liquid carrier, preferably a resin, gum, cellulose or polymerisable monomer.

18. A method according to Claim 17, <u>characterised in that</u> the additive is a water soluble polymerisable substance, the additive being first dissolved in deionised water or other carrier liquid or a mixture to produce a premix solution, and an initiator is added to the dispersion before foaming and a catalyst added after foaming.

19. A method according to Claim 18, <u>characterised in that</u> the addition is carried out a elevated temperature and the catalyst is omitted partially or completely.

20. A dispersion comprising particles in a liquid carrier <u>characterised in that</u> the dispersion has a critical viscosity selected to be below that level at which the introduction of gas cannot take place and above the level at which entrapped gas bubbles will tend to escape.

21. A dispersion according to Claim 20, <u>characterised in that</u> the critical viscosity is from about 5 mPa.s to

about 1000 mPa.s.

22. A dispersion according to Claim 20 or 21, characterised in that the critical viscosity is from about 20 mPa.s to about 250 mPa.s.

23. A dispersion according to any of Claims 20 to 22, characterised in that the average particle size of the particles in the dispersion is less than about 5 micrometres.

24. A dispersion according to Claim 23 characterised in that the average particle size of the particles in the dispersion is less than about 2 micrometres.

25. A dispersion according to any of Claims 20 to 22, characterised in that the average particle size ranges up to about 100 micrometres and agents are present to control undesired settling.

26. A method according to any of Claims 20 to 25, characterised in that content of the solids in the dispersion is about 10% to about 90% by weight, preferably about 40% to about 85% by weight.

27. A dispersion according to any of Claims 20 to 26, characterised in that a deflocculating agent selected to control and maintain gas bubbles is present in the

dispersion.

28. A dispersion according to any of Claims 20 to 27, <u>characterised in that</u> the dispersion contains polymerisable material.

29. A dispersion according to Claim 28, <u>characterised in that</u> the polymerisable material comprises a monomer and an initiator therefor.

30. A dispersion according to Claim 28, <u>characterised in that</u> the polymerisable material is a monosaccharide.

31. A method of making a porous refractory article, the method comprising the steps of:

a) forming a dispersion comprising particles in a liquid carrier;

b) introducing gas into the dispersion; and

c) removing the liquid carrier to provide a solid article having pores derived from the bubbles,

<u>characterised in that</u> the dispersion contains a polymerisable monomeric material.

32. A method according to Claim 31, <u>characterised in that</u> the monomeric material is selected to polymerise by cross

linking.

33. A method according to Claim 31 or 32, characterised in that the monomeric substance is an acrylate.

34. A method according to Claim 31, characterised in that the monomeric substance is a monosaccharide.

35. A method according to any of Claims 31 to 34, characterised in that the average particle size of the particles in the dispersion is less than about 5 micrometres.

36. A method according to Claim 35, characterised in that the average particle size of the particles in the dispersion is less than about 2 micrometres.

37. A method according to any of Claims 31 to 33, characterised in that the average particle distribution ranges up to about 100 micrometres and an agent is present to control undesired settling.

38. A method according to any of Claims 31 to 37, characterised in that content of the solids in the dispersion is about 10% to about 90% by weight, preferably about 40% to about 85% by weight.

39. A method according to any of Claims 31 to 38, characterised in that a gas is introduced into the dispersion by agitation

at high speed.

40. A method according to any of Claims 31 to 39, _characterised in that_ the gas is introduced by bubbling through a filter of defined pore size into the dispersion while being agitated.

41. A method according to Claim 40, _characterised in that_ high pressure gas is forced through a fine filter, then intimately mixed with the dispersion in a suitable chamber and the mixture ejected from a nozzle.

42. A method according to any of Claims 31 to 41, _characterised in that_ the dispersion is housed in a pressurised vessel and gas is injected under pressure into the dispersion t produce a foam when ejected via a nozzle.

43. A method according to any of Claims 31 to 38, _characterised in that_ a gas generating substance is added to the dispersion and caused to generate gas _in situ_.

44. A method according to any of Claims 31 to 43, _characterised in that_ the liquid is removed by drying under reduced pressure.

45. An article comprising a fired porous body comprising bonded refractory particles, _characterised in that_ the body comprises essentially the refractory particles only.

46. An article having green strength comprising a foamed body of bonded refractory particles, characterised in that the article includes a polymerised monomer which will be removed when the article is fired.

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C04B38/00; B01F3/00; C04B35/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C04B ; B01F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	FR,A,1 003 500 (S.A. DES MANUFACTURES DES GLACES ET AL.) 18 March 1952 cited in the application see claims ---	1,4
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 84 (C-572)(3432) 27 February 1989 & JP,A,63 270 368 (OKURA IND CO LTD) 8 November 1988 see abstract ---	31,33, 38,43,46
Y	FR,A,1 573 863 (THE PLESSEY CO LTD) 11 July 1969 see p1, left column, lines 1-5, 17-21 and 36-39; right column, lines 16-19. ---	31,33, 38,43,46

-/--

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
16 NOVEMBER 1992	20. 11. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DAELEMAN P.C.A.

1

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	CHEMICAL ABSTRACTS, vol. 114, no. 6, 11 February 1991, Columbus, Ohio, US; abstract no. 48323g, H. YORITA ET AL. 'Manufacture of high-alumina porous ceramics, and the ceramics obtained' page 333 ; see abstract & JP,A,02 149 482 (H.YORITA) 8 June 1990	45
X	CHEMICAL ABSTRACTS, vol. 112, no. 24, 11 June 1990, Columbus, Ohio, US; abstract no. 222200k, K.NITTA 'Manufacture of high-purity porous ceramics' page 332 ; see abstract & JP,A,01 252 589 (K. NITTA) 9 October 1989	45
X	US,A,3 041 190 (J.S. GRIFFITH ET AL.) 26 June 1962 cited in the application see column 4, line 46 - column 5, line 13 see column 4, line 1 - line 29	1,5,9
A	EP,A,0 130 031 (MATERIALS RESEARCH CORP.) 2 January 1985 see abstract, p.8 lines 21-23, p. 9 lines 1-7 and p.10 lines 14-18.	1,17-19, 31-33,46
A	DE,C,347 057 (J. V. VASS) 8 February 1922 see claim 1	1,14
A	DE,A,3 801 132 (DIDIER-WERKE AG) 27 July 1989 see claim 1	1,13,14
A	DE,A,1 965 008 (OTSUKA KAGAKU YAKUHIN K.K.) 30 July 1970 cited in the application see claim 1	1
A	FR,A,1 482 214 (IPSEN IND.) 26 May 1967 see page 2, left column, line 32 - line 35	
A	EP,A,0 120 243 (IBM) 3 October 1984	

-/--

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 113, no. 26, 24 December 1990, Columbus, Ohio, US; abstract no. 236558r, K. FUTAKI ET AL. 'Manufacture of porous alumina ceramics' page 312 ; see abstract & JP,A,02 229 713 (K. FUTAKI) 12 September 1990	
A	CHEMICAL ABSTRACTS, vol. 112, no. 24, 11 June 1990, Columbus, Ohio, US; abstract no. 222204q, F.ISO 'Manufacture of porous ceramics' page 332 ; see abstract & JP,A,01 242 474 (F. ISO) 27 September 1989	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9201493 SA 63937

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 16/11/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-1003500		None	
FR-A-1573863	11-07-69	None	
US-A-3041190		None	
EP-A-0130031	02-01-85	US-A- 4587068	06-05-86
		CA-A- 1232746	16-02-88
		JP-A- 60042269	06-03-85
DE-C-347057		None	
DE-A-3801132	27-07-89	None	
DE-A-1965008	30-07-70	FR-A- 2028718	16-10-70
		GB-A- 1272010	26-04-72
FR-A-1482214		None	
EP-A-0120243	03-10-84	US-A- 4474731	02-10-84
		JP-B- 1010468	21-02-89
		JP-C- 1523572	12-10-89
		JP-A- 59213678	03-12-84